

## CONTAINER FOR FRAMED PELLICLE

### BACKGROUND OF THE INVENTION

**[0001]** The present invention relates to a container for a framed pellicle or, more particularly, to a container for containing a framed pellicle used for dustproof protection of a photomask in the photolithographic patterning works. In particular, the improvement of the invention is directed to the structure of a pellicle container for containing a framed pellicle used with an object of dustproof protection of a photomask in the patterning works in the manufacture of fine and precision electronic devices including semiconductor devices such as LSIs and VLSIs and liquid crystal display panels.

**[0002]** Photolithographic patterning is a conventional and established technology in the manufacturing process of fine and precision electronic devices including semiconductor devices such as LSIs and VLSIs and liquid crystal display panels. In the photolithographic patterning works, the surface of the substrate for the device is pattern-wise exposed to actinic rays such as ultraviolet light through a pattern-bearing transparency called a photomask. It is very important here that the surface of the photomask is absolutely free from dust particles deposited thereon because the quality of patterning is greatly affected adversely by the dust particles on the photomask due to absorption, scattering and diffraction of the exposure light. In this regard, photolithographic patterning works are conducted in a dust-free atmosphere of a clean room although it is almost impossible to be absolutely free from dust particles even in a clean room of the highest class. A usual procedure therefore is that a framed pellicle for dustproof protection is

mounted on the photomask and the patterning light-exposure is conducted through the transparent pellicle membrane of the framed pellicle.

**[0003]** When the patterning light-exposure is conducted through the pellicle membrane of a framed pellicle mounted on the photomask, dust particles deposited on the surface of the pellicle membrane have no particular adverse effects on the quality of patterning since the exposure light is focused not at the dust particles but at the photomask which is at least several millimeters below the pellicle membrane.

**[0004]** Figure 1 of the accompanying drawing illustrates a vertical cross sectional view of a typical framed pellicle 6 which is an integral device basically consisting of a square or circular frame 3, referred to as a pellicle frame, of a rigid material and a thin and highly transparent film 1, referred to as a pellicle membrane, of a plastic resin spread over one end surface of the pellicle frame 3 and adhesively bonded thereto in a slack-free fashion with intervention of an adhesive layer 2 therebetween. The other end surface of the pellicle frame 3 is usually coated with a pressure-sensitive adhesive forming a pressure-sensitive adhesive layer 4 in order to facilitate mounting of the framed pellicle 6 on the photomask with stability. The surface of the pressure-sensitive adhesive layer 4 is temporarily protected until use by attaching a releasable film or sheet 5.

**[0005]** The plastic resin forming the pellicle membrane 1 is usually selected from nitrocelluloses, cellulose acetates and fluorocarbon polymers in view of their good mechanical strengths even in the form of a thin films and high transparency to the exposure light. A glass plate is also proposed in place of the pellicle membrane 1 of a plastic

resin. The rigid material forming the pellicle frame 3 is usually selected from aluminum, stainless steel, polyethylene and the like. The pellicle membrane 1 is adhesively bonded to one of the end surfaces of the pellicle frame 3 by using an adhesive 2 which can be an acrylic resin-based adhesive, epoxy resin-based adhesive or fluorocarbon resin-based adhesive according to the disclosure in U.S. Patent No. 4,861,402, Japanese Patent Publication No. 58-219023, Japanese Patent Kokai No. 7-168345 and elsewhere. Alternatively, Japanese Patent Kokai No. 58-219023 proposes a bonding method in which an organic solvent having good dissolving power to the plastic resin of the pellicle membrane 1 is applied to the end surface of the pellicle frame 3 followed by partial drying and the pellicle membrane 1 is brought into contact with the end surface of the pellicle frame still adequately wet with the solvent.

**[0006]** The other end surface of the pellicle frame 3, i.e. the end surface opposite to the pellicle membrane 1, is usually provided with a pressure-sensitive adhesive layer 4 by coating with a suitable pressure-sensitive adhesive based on a polybutene resin, polyvinyl acetate resin, acrylic resin or silicone resin. The surface of the pressure-sensitive adhesive layer 4 is temporarily protected until use of the framed pellicle 6 by attaching a releasable sheet or separator 5 which is removed by peeling immediately before the framed pellicle 6 freed from the releasable sheet 5 is mounted on the photomask by gently pressing against the photomask. Needless to say, framed pellicles 6 with the above mentioned releasable sheet 5 are transported and stored as contained in a rigid container for a framed pellicle 6, which is conventionally formed from a plastic resin, in order to protect the same

until use against mechanical damages and contamination.

**[0007]** Turning now to the light for patternwise exposure through the pellicle membrane 1, it is a remarkable trend in recent years to be in compliance with the requirement toward a finer and finer resolution of the photolithographic pattern, the exposure light is under a continuous shift toward those of shorter and shorter wavelengths in order to accomplish the high pattern resolution. For example, the g-line light and I-line light having a wavelength of 436 nm and 365 nm, respectively, which were the major current of the exposure light, now have been replaced with the deep UV light of 248 nm wavelength from a KrF excimer laser which in turn is under replacement with vacuum UV light of 193 nm wavelength from an ArF excimer laser. It is already foreseen that the UV light of a still shorter wavelength of 158 nm such as the fluorine excimer laser beams will be actually employed as the exposure light in photolithographic patterning.

**[0008]** It has unexpectedly become apparent that a very serious problem must be solved in order to conduct the patterning exposure in photolithography by using the above mentioned extremely short-wavelength light as the patterning exposure light. Namely, it is unavoidable that the pellicle membrane 1 made from a plastic resin more or less adsorbs gaseous hydrocarbon compounds and moisture from the atmospheric air and these adsorbates have an effect of decreasing the transmissivity of the pellicle membrane 1 to the exposure light. In addition, these adsorbed gases are activated by the laser irradiation to form initiation sites for the degradation reaction of the plastic resin of the pellicle membrane 1 resulting in a decrease in the durability of the framed pellicle 6.

**[0009]** Since it is usual that the framed pellicles manufactured in a production line are each contained in a plastic-made container and stored for a considerable length of time before the product is transported to the users for actual service, a chance of high possibility for contacting with the above mentioned contaminant gases is given during storage of the framed pellicles in containers. Namely, plastic resins forming the container always contain, though in a trace amount, various organic compounds such as the unpolymerized monomer compounds and organic solvents as the polymerization medium and these organic impurity matters are more or less emitted from the container walls to be adsorbed by the pellicle membrane 1 of the framed pellicle 6 contained in the container and act adversely as described above.

#### SUMMARY OF THE INVENTION

**[0010]** The present invention accordingly has an object to provide, in order to solve the above described problem, a container for a framed pellicle which is free from emission of any organic matters which might be adsorbed on the pellicle membrane of a framed pellicle contained in the container for transportation and/or storage to exhibit the adverse effects of decreasing the light-transmissivity and acceleration of degradation of the pellicle membrane.

**[0011]** Thus, the present invention provides an improvement in a container for a framed pellicle as an assembly of a container base and a covering mountable on the container base jointly to form an inside space for containing a framed pellicle, which improvement comprises forming at least the surface layer of the container base and the covering facing the inside space from an inorganic material selected from

the group consisting of metals, alloys, glass materials and ceramic materials.

**[0012]** While the minimum requirement of the present invention is to form the inner surface layer of the container from an inorganic material, it is optional that the whole bodies of the container base and the covering are formed entirely from an inorganic material or that both of the inner and outer surface layers of the container are formed from an inorganic material.

#### BRIEF DESCRIPTION OF THE DRAWING

**[0013]** Figure 1 is a schematic vertical cross sectional view of a framed pellicle.

**[0014]** Figure 2 is a schematic vertical cross sectional view of an inventive container formed entirely from an inorganic material containing a framed pellicle therein.

**[0015]** Figure 3 is a schematic vertical cross sectional view of an inventive container of which both of the inner and outer surface layers are formed from an inorganic material containing a framed pellicle therein.

**[0016]** Figure 4 is a schematic vertical cross sectional view of an inventive container of which the inner surface layer only is formed from an inorganic material containing a framed pellicle therein.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0017]** As is illustrated in Figure 2, the container 7 of the present invention is an assembly composed of a container base 7A and a covering 7B mountable on the container base 7A. When the covering 7B

is mounted on the container base 7A in place, an inside space 7C is formed to contain the framed pellicle 6.

**[0018]** The most characteristic feature of the inventive container 7 for a framed pellicle is that at least the surface layer of the container 7, i.e. container base 7A and covering 7B, facing the inside space 7C is formed from an inorganic material which can be a metal or alloy, glass material or ceramic material. Examples of the metal and alloy suitable for the purpose include aluminum, copper, iron and stainless steels. The surface of the layers of these metallic materials can be subjected to a variety of surface treatments with an object to improve stability and corrosion resistance. For example, it is optional that the surface of an aluminum layer is subjected to an anodization treatment to form an oxidized thin film thereon. The glass material is not particularly limitative including fused silica glass. The ceramic material used here is exemplified by silicon nitride, silicon carbide, zirconia, alumina, boron nitride and the like.

**[0019]** Instead of forming the entire body of the container 7 from the above mentioned inorganic material as is illustrated in Figure 2, it is optional that the walls of the container have a composite layered structure consisting of a core 8A or 8B made from a conventional plastic resin and cladding layers 9,10 of an inorganic material on the outer and inner surfaces, respectively, of the cores 8A,8B as is illustrated in Figure 3 by a vertical cross sectional view containing a framed pellicle 6 in the inside space. It is of course that the cladding layers 10 of an inorganic material on the outer surface of the container base and covering are not essential and can be omitted as is illustrated in Figure 4 by a vertical cross sectional view containing a framed

pellicle 6. Namely, the inorganic cladding layer 10 is formed only on the surfaces of the container base 8A and covering 8B of a plastic resin facing the inside space 7C to contain the framed pellicle 6.

**[0020]** The inorganic cladding layers 10 on the inner surfaces of the cores 8A,8B of the container should desirably have a thickness of at least 0.1  $\mu$  m. When the thickness is too small, the inorganic cladding layers are eventually subject to the formation of cracks or fissures so that emission of organic contaminant gases from the cores 8A,8B of a plastic resin cannot be completely prevented. The method for forming the inorganic cladding layers 10 on the surfaces of the cores 8A,8B is not particularly limitative depending on the kind of the inorganic materials and desired thickness of the cladding layers 10. For example, the inorganic cladding layers 10 can be formed by the vacuum vapor deposition method or, alternatively, by adhesively bonding a thin sheet of the inorganic material by using an adhesive.

**[0021]** Following is a description of the present invention in more detail by way of Examples and a Comparative Example making reference to the accompanying drawing, which is preceded by the description of the preparation procedure of framed pellicles to be contained in the container.

**[0022]** Thus, a framed pellicle 6A was prepared by adhesively bonding a glass sheet of 1 mm thickness to serve as the pellicle membrane onto one of the end surfaces of an aluminum-made pellicle frame coated with a silicone resin-based adhesive while the other end surface of the pellicle frame was coated with a silicone resin-based pressure-sensitive adhesive in a thickness of 0.5 mm and the pressure-sensitive adhesive layer was protected by attaching a releasable film.

**[0023]** Another framed pellicle 6B was prepared in about the same manner as above excepting for the replacement of the 1 mm thick glass sheet with a 0.5  $\mu$  m thick film of a fluorocarbon resin which was spread over and adhesively bonded to the adhesive-coated end surface of the pellicle frame in a slack-free fashion.

**[0024]** The pellicle membranes of the framed pellicles 6A,6B had transmissions of 80% and 90%, respectively, to the fluorine excimer laser beams of 158 nm wavelength. In the Examples and Comparative Example shown below, these framed pellicles were kept for a length of time in several different pellicle containers and measurements were made for the transmission of the pellicle membranes after storage to the fluorine excimer laser beams.

**[0025]** Example 1.

The framed pellicles 6A,6B prepared as above were each kept in a pellicle container entirely made of aluminum for 1 month at room temperature. The framed pellicles 6A,6B taken out of the respective pellicle containers were subjected to the transmission measurement of the fluorine excimer laser beams to give values of 80% and 90%, respectively, showing no decrease as a consequence of storage.

**[0026]** Example 2.

The experimental procedure was substantially the same as in Example 1 excepting for the replacement of the aluminum-made pellicle containers with containers entirely made from fused silica glass. The transmission values of the pellicle membranes of the framed pellicles 6A,6B after 1 month storage therein were 80% and 90%, respectively, to the fluorine excimer laser beams showing no decrease as a consequence of storage.

**[0027] Example 3.**

The experimental procedure was substantially the same as in Example 1 excepting for the replacement of the aluminum-made pellicle containers with containers made from an ABS resin and provided with a  $0.1 \mu m$  thick cladding layers of aluminum formed by the method of vacuum vapor deposition on the overall surfaces of the container base and covering. The transmission values of the pellicle membranes of the framed pellicles 6A,6B after 1 month storage therein were 80% and 90%, respectively, to the fluorine excimer laser beams showing no decrease as a consequence of storage.

**[0028] Example 4.**

The experimental procedure was substantially the same as in Example 3 except that the  $0.1 \mu m$  thick cladding layers of aluminum were formed only on the inward surfaces of the ABS resin-made container base and covering facing the inside space for containing the framed pellicle. The transmission values of the pellicle membranes of the framed pellicles 6A,6B after 1 month storage therein were 80% and 90%, respectively, to the fluorine excimer laser beams showing no decrease as a consequence of storage.

**[0029] Example 5.**

The experimental procedure was substantially the same as in Example 3 except that the cladding layers on the surfaces of the container base and covering had a double-layered structure consisting of a  $0.5 \mu m$  thick undercladding layer of aluminum and  $0.5 \mu m$  thick top cladding layer of boron nitride each formed by the method of vacuum vapor deposition. The transmission values of the pellicle membranes of the

framed pellicles 6A,6B after 1 month storage therein were 80% and 90%, respectively, to the fluorine excimer laser beams showing no decrease as a consequence of storage.

**[0030] Comparative Example.**

The experimental procedure was substantially the same as in Example 1 excepting for the replacement of the aluminum-made pellicle containers with containers made from a polymethyl methacrylate resin having no inorganic cladding layers thereon. The transmission values of the pellicle membranes of the framed pellicles 6A,6B after 1 month storage therein were 47% and 50%, respectively, to the fluorine excimer laser beams showing remarkable decreases as a consequence of storage.